10:19:44 OCA PAD INITIATION - PROJECT HEADER INFORMATION 09/06/89

Active

Project #: E-21-T31 Cost share #: E-21-343 Rev #: 0
Center # : 10/24-6-R6583-T31 Center shr #: 10/22-1-F6583-T31 OCA file #: 128
Work type : RES
Contract#: F30602-88-D-0025-0031 Mod #: Document : DO
Prime #: Contract entity: GTRC

Subprojects ? : N
Main project #:

Project unit: EE Unit code: 02.010.118
Project director(s):
JOY E B EE (404)894-2936

Sponsor/division names: AIR FORCE / GRIFFISS AFB, NY
Sponsor/division codes: 104 / 023

Award period: 890825 to 900225 (performance) 900325 (reports)

Sponsor amount	New this change	Total to date
Contract value	20,000.00	20,000.00
Funded	20,000.00	20,000.00
Cost sharing amount		2,222.00

Does subcontracting plan apply ?: Y

Title: OPTICAL STUDIES OF POLYMERIC FILMS

PROJECT ADMINISTRATION DATA

OCA contact: Brian J. Lindberg 894-4820

Sponsor technical contact

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Sponsor issuing office

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(315)330-7060
ROME AIR DEVELOPMENT CENTER
DIRECTORATE OF CONTRACTING (PKRM)
GRIFFISS AFB, NY 13441-5700

Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): Y
Defense priority rating : DO-A7 GOV'T supplemental sheet
Equipment title vests with: Sponsor GIT
NONE PROPOSED OR ANTICIPATED.

Administrative comments -
DELIVERY ORDER FULLY FUNDS TASK S-9-7625 (UNIVERSITY OF CALIFORNIA, DAVIS).

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 07/19/90

Project No. E-21-T31 Center No. 10/24-6-R6583-T31

Project Director JOY E B School/Lab ELEC ENGR

Sponsor AIR FORCE/GRIFFISS AFB, NY

Contract/Grant No. F30602-88-D-0025-0031 Contract Entity GTRC

Prime Contract No.

Title OPTICAL STUDIES OF POLYMERIC FILMS

Effective Completion Date 900225 (Performance) 900325 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	
Final Report of Inventions and/or Subcontracts	Y	
Government Property Inventory & Related Certificate	Y	
Classified Material Certificate	Y	
Release and Assignment	Y	
Other	N	

Comments

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	Y
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other	N
	N

NOTE: Final Patent Questionnaire sent to PDPI.

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: JUL-SEP '89

CURRENT QUARTER FUNDING			$476,000.00
DO #	0017	$10,000	
	0026	$15,000	
	0027	$20,000	
	0028	$50,000	
	0029	$40,000	
	0030	$30,000	
	0031	$20,000	
	0032	$66,000	
	0033	$70,000	
	0034	$85,000	
	0035	$70,000	
		$476,000	
CURRENT QUARTER EXPENDITURES			$415,422.69
CONTRACT CEILING			$4,200,000.00
FUNDING TO DATE		-	$2,029,675.00
* PENDING COMMITMENTS		-	$253,994.00
AVAILABLE FUNDING			$1,916,331.00
FUNDING TO DATE			$2,029,675.00
YTD EXPENDITURES		-	$849,451.48
OUTSTANDING EXPENDITURES			$1,180,223.52

* DO #	0007	INCREMENTAL FUNDING	$20,000.00
	0011	INCREMENTAL FUNDING	$19,568.00
	0012	INCREMENTAL FUNDING	$24,700.00
	0015	INCREMENTAL FUNDING	$29,783.00
	0016	INCREMENTAL FUNDING	$31,250.00
	0018	INCREMENTAL FUNDING	$12,000.00
	0019	INCREMENTAL FUNDING	$12,000.00
	0022	INCREMENTAL FUNDING	$54,693.00
	N-0-5703	UNIV OF SOUTHERN FLA/WILSON	$50,000.00
		TOTAL PENDING	$253,994.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: APR-JUN '89

CURRENT QUARTER FUNDING			$160,350.00
DO # 0021	$25,000		
0022	$45,000		
0023	$20,350		
0024	$50,000		
0025	$20,000		
	$160,350		
CURRENT QUARTER EXPENDITURES			$318,963.82
CONTRACT CEILING			$4,200,000.00
FUNDING TO DATE		-	$1,553,675.00
* PENDING COMMITMENTS		-	$718,994.00
AVAILABLE FUNDING			$1,927,331.00
FUNDING TO DATE			$1,553,675.00
YTD EXPENDITURES		-	$434,028.79
OUTSTANDING EXPENDITURES			$1,119,646.21

* DO # 0007	INCREMENTAL FUNDING		$20,000.00
0011	INCREMENTAL FUNDING		$19,568.00
0012	INCREMENTAL FUNDING		$24,700.00
0015	INCREMENTAL FUNDING		$29,783.00
0016	INCREMENTAL FUNDING		$31,250.00
0017	INCREMENTAL FUNDING		$10,000.00
0018	INCREMENTAL FUNDING		$12,000.00
0019	INCREMENTAL FUNDING		$12,000.00
0022	INCREMENTAL FUNDING		$54,693.00
B-9-3621	SRI/LUNT		$20,000.00
N-9-5308	KAMAN SCIENCES		$100,000.00
E-9-7119	DARTMOUTH COLLEGE/CRANE		$100,000.00
N-9-5740	CHRISTIANSON		$15,000.00
N-9-5317	UNIV OF CO/NORGARD		$50,000.00
S-9-7625	UNIV OF CA/DAVIS/KOWELL		$20,000.00
N-9-5314	KAMAN SCIENCES		$100,000.00
N-9-5315	KAMAN SCIENCES		$100,000.00
	TOTAL PENDING		$718,994.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: JAN-MAR '89

CURRENT QUARTER FUNDING			$574,457.00
DO # 0001	$90,729		
0011	$75,000		
0012	$75,000		
0013	$59,989		
0014	$49,989		
0015	$70,000		
0016	$43,750		
0017	$30,000		
0018	$22,000		
0019	$38,000		
0020	$20,000		
	$574,457		
CURRENT QUARTER EXPENDITURES			$86,324.15
CONTRACT CEILING			$4,200,000.00
FUNDING TO DATE		-	$1,393,325.00
* PENDING COMMITMENTS		-	$594,651.00
AVAILABLE FUNDING			$2,212,024.00
FUNDING TO DATE			$1,393,325.00
YTD EXPENDITURES		-	$115,064.97
OUTSTANDING EXPENDITURES			$1,278,260.03

* DO # 0007	INCREMENTAL FUNDING		$20,000.00
0011	INCREMENTAL FUNDING		$19,568.00
0012	INCREMENTAL FUNDING		$24,700.00
0015	INCREMENTAL FUNDING		$29,783.00
0016	INCREMENTAL FUNDING		$31,250.00
0017	INCREMENTAL FUNDING		$10,000.00
0018	INCREMENTAL FUNDING		$12,000.00
0019	INCREMENTAL FUNDING		$12,000.00
C-8-2404	STANFORD UNIV/WIDROW		$100,000.00
N-9-5732	GRIFFIN		$25,000.00
A-9-1476	BOWDOIN COLLEGE/CHONACKY		$20,350.00
E-9-7110	UNIV OF LOWELL/SALES		$50,000.00
S-9-7559	UNIV OF MICHIGAN/ROBINSON		$20,000.00
B-9-3621	SRI/LUNT		$20,000.00
N-9-5308	KAMAN SCIENCES		$100,000.00
E-9-7119	DARTMOUTH COLLEGE/CRANE		$100,000.00
	TOTAL PENDING		$594,651.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: OCT-DEC '88

CURRENT QUARTER FUNDING			$120,834.00
DO # 0004	$66,680		
0006	$54,154		
	$120,834		
CURRENT QUARTER EXPENDITURES			$28,740.82
CONTRACT CEILING			$4,200,000.00
FUNDING TO DATE		-	$818,868.00
* PENDING COMMITMENTS		-	$784,729.00
AVAILABLE FUNDING			$2,596,403.00
FUNDING TO DATE			$818,868.00
YTD EXPENDITURES		-	$28,740.82
OUTSTANDING EXPENDITURES			$790,127.18

* DO # 0001	INCREMENTAL FUNDING		$90,729.00
0007	INCREMENTAL FUNDING		$20,000.00
C-8-2400	STATE UNIV OF NY/FAM		$95,000.00
C-8-2402	RENSSELAER/SAULNER		$100,000.00
B-9-3592	UNIV OF CA/DAVIS/LEVITT		$60,000.00
N-9-5514	SOHAR INC./HECHT		$50,000.00
C-9-2015	NCS/O'NEAL		$100,000.00
A-9-1120	HITEC, INC./KAZAKOS		$75,000.00
E-9-7057	UNIV OF TX/ARLINGTON/FUNG		$40,000.00
E-9-7093	MONTANA STATE/JOHNSON		$34,000.00
S-9-7552	ALFRED UNIV/SYNDER		$20,000.00
C-9-2404	STANFORD UNIV/WIDROW		$100,000.00
	TOTAL PENDING		$784,729.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: JUL-SEPT '88

CURRENT QUARTER FUNDING			$698,034.00
DO # 0001	$56,000		
0002	$95,141		
0003	$78,854		
0004	$230,000		
0005	$45,561		
0006	$25,000		
0007	$20,000		
0008	$98,374		
0009	$29,403		
0010	$19,701		
	$698,034		
CURRENT QUARTER EXPENDITURES			$0.00
CONTRACT CEILING			$4,200,000.00
FUNDING TO DATE		-	$698,034.00
* PENDING COMMITMENTS		-	$426,563.00
AVAILABLE FUNDING			$3,075,403.00
FUNDING TO DATE			$698,034.00
YTD EXPENDITURES		-	$0.00
OUTSTANDING EXPENDITURES			$698,034.00

* DO # 0001	INCREMENTAL FUNDING		$90,729.00
0002	INCREMENTAL FUNDING		$66,680.00
0003	INCREMENTAL FUNDING		$54,154.00
0004	INCREMENTAL FUNDING		$20,000.00
C-8-2400	STATE UNIV OF NY/FAM		$95,000.00
C-8-2402	RENSSELAER/SAULNER		$100,000.00
TOTAL PENDING			$426,563.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: MAY-JUN '88

CURRENT QUARTER FUNDING		$0.00
CURRENT QUARTER EXPENDITURES		$0.00
CONTRACT CEILING		$4,200,000.00
FUNDING TO DATE	-	$0.00
* PENDING COMMITMENTS	-	$766,000.00
AVAILABLE FUNDING		$3,434,000.00
FUNDING TO DATE		$0.00
YTD EXPENDITURES	-	$0.00
OUTSTANDING EXPENDITURES		$0.00

*	C-8-2120 WESTINGHOUSE/BEAUDET	$56,000.00
	C-8-2129 RENSSELAER/DAS	$100,000.00
	E-8-7066 UNIV OF PENN/STEINBERG	$100,000.00
	E-8-7124 BOSTON COLLEGE/McFADDEN	$35,000.00
	E-8-7125 BRANDEIS UNIV/HENCHMAN	$23,000.00
	E-8-7126 PENN STATE/CASTLEMAN	$22,000.00
	A-8-1631 UNIV OF PENN/STEINBERG	$100,000.00
	B-8-3617 GA WASHINGTON UNIV/MELTZER	$100,000.00
	B-8-3618 GA WASHINGTON UNIV/BERKOVICH	$100,000.00
	C-8-2492 GA TECH/SMITH	$50,000.00
	A-8-1203 GA TECH/HUGHES	$80,000.00
	TOTAL PENDING	$766,000.00

L 21-731

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: OCT-DEC '89

CURRENT QUARTER FUNDING				$292,994.00
DO #	0001	$9,000	C-8-2129	
	0011	$19,568	C-8-2400	
	0012	$24,700	C-8-2402	
	0015	$29,783	C-9-2015	
	0016	$31,250	A-9-1120	
	0018	$12,000	E-9-7093	
	0019	$62,000	C-9-2109	
	0022	$54,693	C-9-2404	
	0028	$50,000	N-9-5308	
		$292,994		

CURRENT QUARTER EXPENDITURES		$286,691.16
CONTRACT CEILING		$4,200,000.00
FUNDING TO DATE	-	$2,322,669.00
* PENDING COMMITMENTS	-	$595,000.00
AVAILABLE FUNDING		$1,282,331.00
FUNDING TO DATE		$2,322,669.00
YTD EXPENDITURES	-	$1,136,142.64
OUTSTANDING EXPENDITURES		$1,186,526.36

*	DO # 0007	S-8-7592	INCREMENTAL FUNDING	$20,000.00
	0029	E-9-7119	INCREMENTAL FUNDING	$60,000.00
	0030	N-9-5317	INCREMENTAL FUNDING	$20,000.00
	0034	N-9-5314	INCREMENTAL FUNDING	$15,000.00
	0016	N-9-5315	INCREMENTAL FUNDING	$30,000.00
	N-0-5703	UNIV OF SOUTHERN FLA/WILSON		$50,000.00
	A-0-1102	UNIV OF CA/SMOOT, BARBER, GT		$100,000.00
	P-0-6011	NCSU/VANDERLUGT		$100,000.00
	C-0-2456	NEW JERSEY INST/BAR-NESS		$100,000.00
	P-0-6014	STEVENS INST/ZMUDA		$100,000.00
	TOTAL PENDING			$595,000.00

WAITING FOR PROPOSALS:
P-0-6018 UAH/CAULFIELD
P-0-6021 GT/SUMNERS
P-0-6022 CORNELL UNIV/TANG
B-0-3353 ROCHESTER INST/LASKY

ROME AIR DEVELOPMENT CENTER
EXPERT SCIENCE AND ENGINEERING PROGRAM
CONTRACT NO. F30602-88-D-0025

R & D STATUS REPORT

PERIOD COVERED: August 1, 1989 - December 31, 1989

TASK NUMBER: S-9-7625

TITLE: Optical Studies of Polymeric Films

PRINCIPAL INVESTIGATOR: Stephen T. Kowel

INSTITUTION: University of California, Davis

OTHER PARTICIPANTS AND TITLES: Andre Knoesen, Co-Principal Investigator
Brian Anderson, Post Graduate Research Engineer
M. A. Mortazavi, Post Graduate Research Engineer
C. Eldering, Post Graduate Research Engineer
B. Higgins, Co-Principal Investigator

A. TECHNICAL PROGRESS ACHIEVED ON EFFORT: (See Attachment)

B. TRAVEL: None

C. PRESENTATIONS AND PUBLICATIONS:

None as yet

D. LEVEL OF EFFORT BY EACH CONTRIBUTOR (IN MAN-MONTHS OR MAN-HOURS)

A. Knoesen, 1 person-month
B. Anderson, 0.4 person-month
M. A. Mortazavi, 1 person-month
C. Eldering, 0.7 person-month

OPTICAL STUDIES OF POLYMERIC FILMS

FINAL REPORT
U. S. Air Force Contract F30602-88-D-0025, Task S-9-7625

8/89 - 12/89

submitted to the
Georgia Institute of Technology

by the

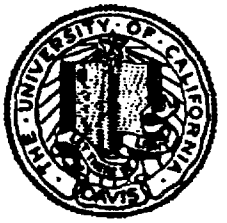
Department of Electrical Engineering and Computer Science
University of California, Davis

Stephen T. Kowel André Knoesen, and Brian G. Higgins
Principal Investigators

and

M. A. Mortazavi, C. A. Eldering, and B. Anderson

March, 1990



OPTICAL STUDIES OF POLYMERIC FILMS

A. TECHNICAL PROGRESS ACHIEVED IN EFFORT

A.1 INTRODUCTION

Organic molecules possess second order nonlinearities ($\chi^{(2)}$ processes) orders of magnitude larger than observed in inorganic solids, and third order nonlinearities ($\chi^{(3)}$ processes) as large as any inorganic crystal (with the exception of GaAs at its absorption bandedge). Thus technical applications (electro-optical modulation, second harmonic generation, signal manipulation in fiber systems, etc.) might be accomplished or improved with thin film overlays. For example, the large $\chi^{(2)}$ will decrease interaction distances eliminating the need for phase matching in second harmonic generation (SHG). Unlike inorganic crystals, polymer films can provide topographic coverage on a variety of substrates, including silicon integrated circuits and linear waveguides. This will enable considerable increase in functional integration, providing global optical interconnects for silicon integrated circuits, as well as nonlinear functional elements for planar optical waveguides. As a topographic overlay on a memory chip, an array of etalons with electro-optic film spacers could provide a means to broadcast the entire contents of the memory to one, or to many, processors without contention.[1] A multiprocessor architecture employing such a global, fixed interconnect has been described.[2] The application of such an overlay could also be important for a system of reconfigurable interconnects.[3]

The challenge is to fabricate thin films capable of evincing the extraordinary optical performance promised by the molecular design while enduring realistic environmental conditions. The global thrust of research now confirms the validity of our strategy for obtaining useful materials - combining the optically active chromophore with polymers for robustness. Langmuir-Blodgett deposition offers an excellent opportunity for developing interesting film systems possessing a high level of alignment uniformity (for $\chi^{(2)}$ effects) and excellent optical quality at reasonable cost, durably bonded to any one of the substrate materials of choice (silicon, $LiNbO_3$, GaAs, etc.).

We have also made significant progress on fabricating spin-coated films of dye substituted polymers with the required noncentrosymmetry induced by a novel corona poling technique. This technique has already produced materials used to demonstrate femtosecond second harmonic pulse autocorrelation [4] as well as electro-optical modulation in a Fabry-Perot etalon.[5] The nonlinear properties of these films stabilize at a useful level and withstand practical power levels of order 1 GW/cm^2. These 'existence proofs' offer great encouragement that these are useful materials which can occupy a unique niche. We have demonstrated that these films are relatively inexpensive to produce, can cover large

areas, can be tailored for specific absorption characteristics, and can be processed to stabilize the nonlinear property of interest.

We have conducted research involving nonlinear polymeric thin films related to the relationships among molecular properties, thin film deposition and processing techniques, the long term structure, and properties of deposited systems. By focussing on polymers, we expect to create robust materials with stable nonlinear properties capable of standing up to the demands of practical applications. Through the use of the Langmuir-Blodgett (LB) deposition technique, we have the capability to manipulate and engineer materials on a monomolecular level. Poled films deposited by spin coating techniques offer the opportunity to engineer thicker films. These studies will enable us to compare deposition strategies in order to determine their relative strengths and weaknesses, to understand the role of molecular architecture in influencing film properties, and to further improve the molecular design.

A.2 LANGMUIR-BLODGETT FILMS

Langmuir-Blodgett (LB) films are prepared by depositing a small amount of material, dissolved in a volatile solvent, onto the surface of a liquid. This liquid is usually highly purified water, and is referred to as the subphase. Successful deposition requires the material to be insoluble in the subphase. After evaporation of the solvent, the spread material, referred to as the Langmuir layer, is in a two-dimensional "gaseous" state, and must be compressed to form a "solid" film. This is accomplished by imposing a surface pressure on the layer using a movable barrier. The LB trough consists of the subphase container, movable barrier, and a film balance. The film balance, as developed by Langmuir, measures the two-dimensional surface pressure (π) through a determination of the differential surface tension. As the area of the film is decreased, the monolayer may undergo a series of phase transitions from a dilute "gas" to a "liquid", and finally to a condensed "solid". In the condensed phase the molecules are packed together with some orientational order. For long chain fatty acids, this structure is similar to that of a smectic liquid crystal, with the chains aligned nearly normal to the subphase surface. In the gaseous and liquid phases the molecular chains may be disordered. Since the original reports by Blodgett and Langmuir, a wide variety of materials have been deposited as LB films, including fatty acids, fatty alcohols, fatty esters, fatty amines, porphyrins, chlorophyll, and proteins. In the last decade there has been a large resurgence of interest in the LB technique because of its molecular engineering capability to build ordered ultrathin films. The technique offers a unique control of thickness, composition, and structure of

the film. For polymeric materials with large optical nonlinearities, the LB technique may offer the ultimate in chemical design flexibility.

In this research project the SHG from LB mono- and multilayer films made of stilbazolium-PECH, a stilbazolium-substituted polyether, was shown to be influenced by the number of optically inactive behenate layers, N_B, deposited between the glass substrate and the first dye layer. For monolayers of stilbazolium-PECH, the SHG monotonically decreased as N_B increased, up to about 6 or 8 buffer layers, while further buffer layer deposition did not appreciably change the SHG. There was a small blue shift in the wavelength of peak absorption for the dye monolayer UV-VIS absorption spectra as N_B increased. The SHG enhancement of multilayer dye films, made by interleaving stilbazolium-PECH with behenate, was strongly influenced by the thickness of the behenate buffer layer. When an interleaved dye film was deposited on a fourteen layer behenate buffer, the SHG enhancement was quadratic ($I^{2\omega} \propto n^2$) with the number of dye layers, n, deposited. However, when an interleaved LB dye film was deposited directly on glass, the enhancement was only near quadratic for about the first five dye layers and for more dye layers deposited the enhancement was linear. As more buffer layers were deposited, the SHG enhancement for the interleaved stilbazolium-PECH multilayer films increased, especially for the first ten dye layers. The SHG enhancement had a quadratic increase with the number of dye layers deposited (up to $N_B = 89$) when eight or more behenate buffer layers were used.

A.3 POLED POLYMERS

Spin-coating is a classic method of fabricating polymer films. This method is particularly well suited to quickly fabricating thicker films (> 1 μm). Recently, our group[6] and others have recognized that this simple technique can be used to create films evincing large second order nonlinearities provided that electric field poling is applied in such a manner as to impose long term orientational order. Polymeric films with large macroscopic second order nonlinear properties can be fabricated by permanently orienting molecular components with large hyperpolarizability within a polymer host. One method is to deposit a film consisting of randomly oriented nonlinear dye molecules embedded in a host polymer which are then oriented by the application of an external electric field. Various poling techniques do exist to produce optical nonlinear films. In particular, corona-onset poling at elevated temperatures (COPET) has been shown to be very effective in achieving large orientational order in thin polymeric films. The increased stability of the nonlinear chromophore in the side-chain polymer leads to substantial improvement in both magnitude and stability of the second order nonlinear properties compared to mixture film systems.

COPET induces electric fields ≈ 2 MV/cm, twice that of parallel plate poling, and thus greater alignment. Also, corona poling is done without electrodes on the film and therefor is compatible with many optical probes.

In this research project second order nonlinear properties of COPET side-chain and mixture films of coumaromethacrylate polymeric films were investigated. The enhancement of second order properties of coumaromethacrylate side-chain polymers with increasing dye concentration was examined. It was found that in the poling process involving the side-chain polymer films both the temperature and electric field strength are important parameters and a therefor careful optimization of these poling parameters will result in significant improvement in the second order optical nonlinearities. From the spectroscopic absorption measurements of corona-onset poled and unpoled films, the orientational order, and an estimation of the magnitude of the effective internal electric field present in the films due to the poling process are obtained. CMA-MMA mixtures reach their maximum attainable order at poling temperatures ≈ T_g. In side-chain polymers, the increased structural rigidity necessitates poling temperatures ≈ 50 ^{o}C above the glass transition temperature.

References

1 C. A. Eldering, S. T. Kowel, M. A. Mortazavi, and P. Brinkley, accepted for *Applied Optics*, Special Issue on Optical Interconnects (March, 1989).

2 N. Matloff, S. T. Kowel, and C. Eldering, *Proceedings of the 1988 ACM International Conference on Supercomputing*, St.-Malo, France, 16 (1988).

3 C.A. Eldering, S. T. Kowel, P. F. Brinkley, N. Matloff, T. Schubert, and R. Gosula, *Proceedings of the SPIE 33rd Annual International Symposium on Optical and Optoelectronic Applied Science and Engineering*, 1151 (1989).

4 M. A. Mortazavi, D. Yankelevich, A. Knoesen, A. Dienes, S. T. Kowel, and S. Dijaili, *Applied Optics*, 28, 3278 (1989).

5 C. A. Eldering, S. T. Kowel, and A. Knoesen, *Applied Optics*, 28, 4442, (1989).

6 M.A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins, and A. Dienes, *JOSA B*, 6, 733 (1989).

OPTICAL STUDIES OF POLYMERIC FILMS

FINAL REPORT
U. S. Air Force Contract F30602-88-D-0025, Task S-9-7625

8/89 - 12/89

submitted to the
Georgia Institute of Technology

by the

Department of Electrical Engineering and Computer Science
University of California, Davis

Stephen T. Kowel André Knoesen, and Brian G. Higgins
Principal Investigators

and

M. A. Mortazavi, C. A. Eldering, and B. Anderson

March, 1990

OPTICAL STUDIES OF POLYMERIC FILMS

A. TECHNICAL PROGRESS ACHIEVED IN EFFORT

A.1 INTRODUCTION

Organic molecules possess second order nonlinearities ($\chi^{(2)}$ processes) orders of magnitude larger than observed in inorganic solids, and third order nonlinearities ($\chi^{(3)}$ processes) as large as any inorganic crystal (with the exception of GaAs at its absorption bandedge). Thus technical applications (electro-optical modulation, second harmonic generation, signal manipulation in fiber systems, etc.) might be accomplished or improved with thin film overlays. For example, the large $\chi^{(2)}$ will decrease interaction distances eliminating the need for phase matching in second harmonic generation (SHG). Unlike inorganic crystals, polymer films can provide topographic coverage on a variety of substrates, including silicon integrated circuits and linear waveguides. This will enable considerable increase in functional integration, providing global optical interconnects for silicon integrated circuits, as well as nonlinear functional elements for planar optical waveguides. As a topographic overlay on a memory chip, an array of etalons with electro-optic film spacers could provide a means to broadcast the entire contents of the memory to one, or to many, processors without contention.[1] A multiprocessor architecture employing such a global, fixed interconnect has been described.[2] The application of such an overlay could also be important for a system of reconfigurable interconnects.[3]

The challenge is to fabricate thin films capable of evincing the extraordinary optical performance promised by the molecular design while enduring realistic environmental conditions. The global thrust of research now confirms the validity of our strategy for obtaining useful materials - combining the optically active chromophore with polymers for robustness. Langmuir-Blodgett deposition offers an excellent opportunity for developing interesting film systems possessing a high level of alignment uniformity (for $\chi^{(2)}$ effects) and excellent optical quality at reasonable cost, durably bonded to any one of the substrate materials of choice (silicon, $LiNbO_3$, GaAs, etc.).

We have also made significant progress on fabricating spin-coated films of dye substituted polymers with the required noncentrosymmetry induced by a novel corona poling technique. This technique has already produced materials used to demonstrate femtosecond second harmonic pulse autocorrelation [4] as well as electro-optical modulation in a Fabry-Perot etalon.[5] The nonlinear properties of these films stabilize at a useful level and withstand practical power levels of order 1 GW/cm2. These 'existence proofs' offer great encouragement that these are useful materials which can occupy a unique niche. We have demonstrated that these films are relatively inexpensive to produce, can cover large

areas, can be tailored for specific absorption characteristics, and can be processed to stabilize the nonlinear property of interest.

We have conducted research involving nonlinear polymeric thin films related to the relationships among molecular properties, thin film deposition and processing techniques, the long term structure, and properties of deposited systems. By focussing on polymers, we expect to create robust materials with stable nonlinear properties capable of standing up to the demands of practical applications. Through the use of the Langmuir-Blodgett (LB) deposition technique, we have the capability to manipulate and engineer materials on a monomolecular level. Poled films deposited by spin coating techniques offer the opportunity to engineer thicker films. These studies will enable us to compare deposition strategies in order to determine their relative strengths and weaknesses, to understand the role of molecular architecture in influencing film properties, and to further improve the molecular design.

A.2 LANGMUIR-BLODGETT FILMS

Langmuir-Blodgett (LB) films are prepared by depositing a small amount of material, dissolved in a volatile solvent, onto the surface of a liquid. This liquid is usually highly purified water, and is referred to as the subphase. Successful deposition requires the material to be insoluble in the subphase. After evaporation of the solvent, the spread material, referred to as the Langmuir layer, is in a two-dimensional "gaseous" state, and must be compressed to form a "solid" film. This is accomplished by imposing a surface pressure on the layer using a movable barrier. The LB trough consists of the subphase container, movable barrier, and a film balance. The film balance, as developed by Langmuir, measures the two-dimensional surface pressure (π) through a determination of the differential surface tension. As the area of the film is decreased, the monolayer may undergo a series of phase transitions from a dilute "gas" to a "liquid", and finally to a condensed "solid". In the condensed phase the molecules are packed together with some orientational order. For long chain fatty acids, this structure is similar to that of a smectic liquid crystal, with the chains aligned nearly normal to the subphase surface. In the gaseous and liquid phases the molecular chains may be disordered. Since the original reports by Blodgett and Langmuir, a wide variety of materials have been deposited as LB films, including fatty acids, fatty alcohols, fatty esters, fatty amines, porphyrins, chlorophyll, and proteins. In the last decade there has been a large resurgence of interest in the LB technique because of its molecular engineering capability to build ordered ultrathin films. The technique offers a unique control of thickness, composition, and structure of

the film. For polymeric materials with large optical nonlinearities, the LB technique may offer the ultimate in chemical design flexibility.

In this research project the SHG from LB mono- and multilayer films made of stilbazolium-PECH, a stilbazolium-substituted polyether, was shown to be influenced by the number of optically inactive behenate layers, N_B, deposited between the glass substrate and the first dye layer. For monolayers of stilbazolium-PECH, the SHG monotonically decreased as N_B increased, up to about 6 or 8 buffer layers, while further buffer layer deposition did not appreciably change the SHG. There was a small blue shift in the wavelength of peak absorption for the dye monolayer UV-VIS absorption spectra as N_B increased. The SHG enhancement of multilayer dye films, made by interleaving stilbazolium-PECH with behenate, was strongly influenced by the thickness of the behenate buffer layer. When an interleaved dye film was deposited on a fourteen layer behenate buffer, the SHG enhancement was quadratic ($I^{2\omega} \propto n^2$) with the number of dye layers, n, deposited. However, when an interleaved LB dye film was deposited directly on glass, the enhancement was only near quadratic for about the first five dye layers and for more dye layers deposited the enhancement was linear. As more buffer layers were deposited, the SHG enhancement for the interleaved stilbazolium-PECH multilayer films increased, especially for the first ten dye layers. The SHG enhancement had a quadratic increase with the number of dye layers deposited (up to $N_B = 89$) when eight or more behenate buffer layers were used.

A.3 POLED POLYMERS

Spin-coating is a classic method of fabricating polymer films. This method is particularly well suited to quickly fabricating thicker films (> 1 μm). Recently, our group[6] and others have recognized that this simple technique can be used to create films evincing large second order nonlinearities provided that electric field poling is applied in such a manner as to impose long term orientational order. Polymeric films with large macroscopic second order nonlinear properties can be fabricated by permanently orienting molecular components with large hyperpolarizability within a polymer host. One method is to deposit a film consisting of randomly oriented nonlinear dye molecules embedded in a host polymer which are then oriented by the application of an external electric field. Various poling techniques do exist to produce optical nonlinear films. In particular, corona-onset poling at elevated temperatures (COPET) has been shown to be very effective in achieving large orientational order in thin polymeric films. The increased stability of the nonlinear chromophore in the side-chain polymer leads to substantial improvement in both magnitude and stability of the second order nonlinear properties compared to mixture film systems.

COPET induces electric fields ≈ 2 MV/cm, twice that of parallel plate poling, and thus greater alignment. Also, corona poling is done without electrodes on the film and therefor is compatible with many optical probes.

In this research project second order nonlinear properties of COPET side-chain and mixture films of coumaromethacrylate polymeric films were investigated. The enhancement of second order properties of coumaromethacrylate side-chain polymers with increasing dye concentration was examined. It was found that in the poling process involving the side-chain polymer films both the temperature and electric field strength are important parameters and a therefor careful optimization of these poling parameters will result in significant improvement in the second order optical nonlinearities. From the spectroscopic absorption measurements of corona-onset poled and unpoled films, the orientational order, and an estimation of the magnitude of the effective internal electric field present in the films due to the poling process are obtained. CMA-MMA mixtures reach their maximum attainable order at poling temperatures ≈ T_g. In side-chain polymers, the increased structural rigidity necessitates poling temperatures ≈ 50 ^{o}C above the glass transition temperature.

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